



(11) (A) No. 1 2 0 9 3 6 1

(45) ISSUED 860812

(52) CLASS 71-41
C.R. CL. 167-4.1

⁴
(51) INT. CL. A01N 25/04

(19) (CA) **CANADIAN PATENT** (12)

(54) Microemulsions

(72) Hausmann, Heinz;
Niessen, Heinz-Josef;
Horstmann, Heinz-Otto,
Germany (Federal Republic of)

(73) Granted to Bayer Aktiengesellschaft
Germany (Federal Republic of)

(21) APPLICATION No. 437,476

(22) FILED 830923

(30) PRIORITY DATE Germany (Federal Republic of)
(P 32 35 612.9) 820925

No. OF CLAIMS 18 - NO DRAWING

1209361

- 1 -

The present invention relates to aqueous micro-emulsions of agrochemical active compounds and/or active compounds for combating pests in the domestic and hygiene sectors. The invention also relates to a process for the
5 preparation of these microemulsions and to their use.

Oil-in-water emulsions of numerous agrochemical active compounds of low solubility in water are already known; in addition to the active compounds, these
10 emulsions also contain, in each case, either a surface-active substance and a thickener or else a relatively large quantity of surface-active substances (compare DE-A (German Published Specification) 3,009,944, DE-A (German Published Specification) 3,011,611 and JP-A
15 (Japanese Published Specification) 122,628-77). This addition of thickeners or of large quantities of surfactant is associated with additional expense and thus constitutes a serious disadvantage of the known oil-in-water emulsions. In addition to this, the preparation which
20 has hitherto been described of emulsions of this type is not generally applicable. This is because, essentially, it is possible to emulsify by this process only those active compounds of low solubility in water which are liquid at room temperature or at least have a very low
25 melting point. It is also disadvantageous that the known oil-in-water emulsions are frequently not adequately stable under cold conditions and that, in some cases, forced emulsification using homogenisers is required.

Aqueous microemulsions which contain
30 - 0.1 to 80% by weight of at least one agrochemical active compound of low solubility in water and/or one active compound for combating pests in the household and hygiene sectors,

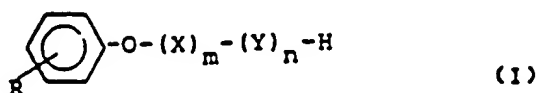
Le A 21 929



1209361

- 2 -

1 to 20% by weight of a mixture of emulsifiers
consisting of
a) at least one alkylaryl polyglycol ether of the
formula



in which

R represents alkyl having 8 to 20 carbon
atoms,

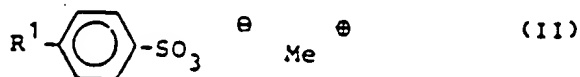
X and Y each represent a $-\text{CH}_2-\text{CH}_2-\text{O}-$,
 $-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{O}-$ or $-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{O}-$ group, but X and Y

do not simultaneously represent an oxyethylene
or oxypropylene unit,

m represents numbers from 10 to 45 and

n represents numbers from 10 to 45, and

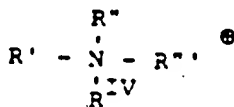
at least one alkylarylsulphonic acid salt of the
formula



in which

R¹ represents alkyl having 8 to 35 carbon
atoms and

Me[⊕] represents an alkali metal cation, an
equivalent of an alkaline earth metal cation
or a cation of the formula



herein

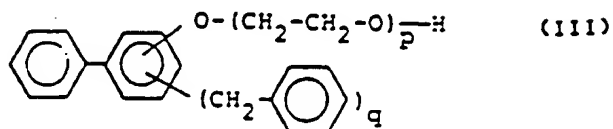
R¹, R^{II}, R^{III} and R^{IV} independently of one

1209361

- 3 -

another represent hydrogen, alkyl having 1 to 4 carbon atoms or hydroxyalkyl having 1 to 4 carbon atoms, or

b) at least one alkylaryl polyglycol ether of the formula

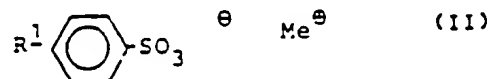


in which

p represents numbers from 5 to 20 and

q represents numbers from 1 to 3, and

at least one alkylarylsulphonic acid salt of the formula



in which

R¹ and Me[⊕] have the meaning indicated above,

15

- and also water and
- if appropriate, 1 to 30% by weight of at least one organic solvent of low miscibility with water and/or of a solubiliser and also,
- 20 - if appropriate, 0.1% to 15% by weight of additives, the sum of the components being in each case 100% by weight, have been found.

It has also been found that the microemulsions according to the invention can be prepared by adding, while stirring, to water optionally containing additives, a homogeneous mixture consisting of

25

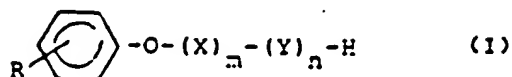
- at least one agrochemical active compound of low solubility in water and/or one active compound for combating pests in the household and hygiene

Le A 21 929

sectors,

a mixture of emulsifiers consisting of

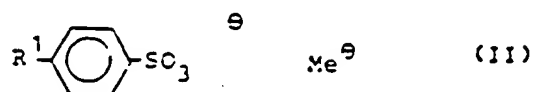
a) at least one alkylaryl polyglycol ether of the
5 formula



in which

R, X, Y, m and n have the meaning indicated
above, and

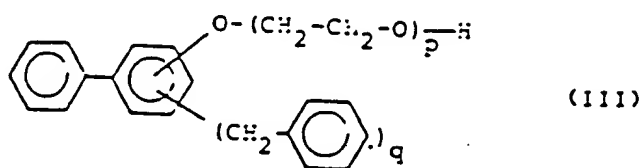
10 at least one alkylarylsulphonic acid salt of the
formula



in which

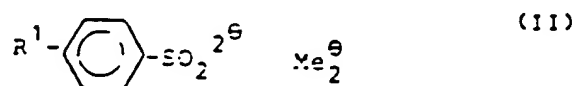
R¹ and Me⁺ have the meaning indicated above,
15 or

b) at least one alkylaryl polyglycol ether of the
formula



in which

20 p and q have the meaning indicated above, and
at least one alkylarylsulphonic acid salt of the
formula



1209361

- 5 -

in which

- R¹ and Me^② have the meaning indicated above,
if appropriate, at least one organic solvent of
low miscibility with water and/or a solubiliser,
5 and also,
- if appropriate, additives.

Finally, it has been found that - depending on
the active compounds they contain - the microemulsions
according to the invention can be used for various pur-
10 poses in agriculture or horticulture, or in the household
and hygiene sectors.

It must be described as extremely surprising that
the microemulsions according to the invention are stable,
since it would have been expected on the basis of the
15 known state of the art that emulsions of this type, which
contain no thickeners and also only a small proportion of
surfactant, would not be stable for a prolonged period.
Thus it is apparent from DE-A (German Published Specifi-
cation) 3,009,944 and DE-A (German Published Specification)
20 3,011,611 that the oil-in-water emulsions described in
those texts necessarily contain a thickener as a stabili-
ser. The emulsions disclosed in JP-A (Japanese Published
Specification) 122,628-77 have a very high proportion
of surfactant in relation to the quantity of active com-
25 pound. The excellent stability of the microemulsions
according to the invention could not, therefore, have been
foreseen.

The microemulsions according to the invention are
distinguished by a number of advantages. Thus the expen-
30 sive addition of thickeners or large quantities of emulsi-
fiers is not necessary in their preparation. Furthermore,
these emulsions contain either only an extremely small
quantity of organic solvents or none at all. Therefore,
they are incombustible and free, or at least virtually
35 free, from odour troubles caused by organic solvents, and
have a lower toxicity or phytotoxicity than corresponding
Le A 21 929

formulations containing organic solvents in the concentrations otherwise customary. In addition, the microemulsions according to the invention are stable under the conditions which prevail in practice. When stored for
5 long periods, these emulsions remain unchanged both at temperatures of 50°C and at low temperatures. Finally, the microemulsions according to the invention can be prepared in a simple manner. Forced emulsification using homogenisers is not necessary. In addition, a very considerable advantage consists in the fact that active com-
10 pounds of low solubility in water which are solid or liquid at room temperature can be emulsified with equal ease. Furthermore, the microemulsions according to the invention have a relatively low viscosity, so that accurate metering presents no difficulties. Finally, the microemulsions
15 according to the invention are completely transparent preparations which can be diluted without problems in any desired ratio with water before use, stable, sprayable formulations being thus formed.

20 The microemulsions according to the invention contain at least one agrochemical active compound of low solubility in water and/or one active compound for combating pests in the household and hygiene sectors. These active compounds are present in the liquid state in the
25 oil phase.

Suitable active compounds are substances which are liquid at room temperature, as well as those which are solid at room temperature. The only requirement for liquid active compounds is that they should be sparingly
30 soluble in water. Compounds of this type are to be understood here as meaning substances which are soluble to the extent of not more than 0.5% by weight in water at 20°C. Solid active compounds must, however, additionally be
35 adequately soluble in an organic solvent of low miscibility with water and/or in a solubiliser.

Agrochemical substances are to be understood in
Le A 21 929

1209361

- 7 -

- the present case as meaning any active compounds which can customarily be used in plant protection. These include, for example, insecticides, acaricides, nematocides, fungicides, herbicides, growth regulators and fertilisers. The following may be mentioned as individual examples of active compounds of this type:
- 0,0-diethyl 0-(4-nitrophenyl) thionophosphate,
0,0-dimethyl 0-(4-nitrophenyl) thionophosphate,
0-(ethyl) 0-(4-methylthiophenyl) S-propyl dithiophosphate,
10 (0,0-diethylthionophosphoryl)- α -oximinophenylacetonitrile,
2-isopropoxyphenyl N-methylcarbamate,
3-methylthio-4-amino-6-tert.-butyl-1,2,4-triazin-5-one,
3-methylthio-4-isobutylideneamino-6-tert.-butyl-1,2,4-triazin-5-one,
15 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine,
2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate,
3,5-dimethyl-4-methylthiophenyl N-methylcarbamate,
0,0-diethyl 0-(3-chloro-4-methyl-7-coumarinyl) thiophosphate,
20 6,7,8,9,10,10-hexachloro-1,5,5A,6,9,9A-hexahydro-6,9-methane-2,3,4-benzodioxathiepin-3-oxide,
1,4,5,6,7,8,8-heptachloro-4,7-endomethylene-3A,4,7,7A-tetrahydroindene,
2-(2-furyl)-benzimidazole,
25 5-amino-1-bis-(dimethylamido)-phosphoryl-3-phenyl-1,2,4-triazole,
4-hydroxy-3-(1,2,3,4-tetrahydro-1-naphthyl)-coumarin,
S-[1,2-bis-(ethoxycarbonyl)-ethyl] 0,0-dimethyl dithiophosphate,
30 0,0-dimethyl 0-(4-methylmercapto-3-methylphenyl) thionophosphate,
0-ethyl-0-(2-isopropoxycarbonylphenyl)-N-isopropylthionophosphoric acid ester-amide,
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-
35 2-butanone,
(S)- α -cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dibromovinyl)-
Le A 21 929

1209361

- 8 -

2,2-dimethylcyclopropanecarboxylate and
α-cyano-3-phenoxy-4-fluorobenzyl 2,2-dimethyl-3-(β,β-dichloro-
* vinyl)-cyclopropanecarboxylate.

Active compounds for combating pests in the domestic
and hygiene sectors are to be understood, in the present case, as
meaning any customary active compounds of low solubility in water
which are suitable for indications of this type. The following
may be mentioned as individual examples of active compounds of
this type:

10 2-isopropoxyphenyl N-methylcarbamate,
0,0-diethyl 0-(4-nitrophenyl) thionophosphate,
0,0-dimethyl 0-(4-nitrophenyl) thionophosphate,
s-[1,2-bis-(ethoxycarbonyl)-ethyl] 0,0-dimethyl dithiophosphate,
0,0-dimethyl 0-(3-methyl-4-nitrophenyl) thionophosphate,
0,0-dimethyl 0-(4-methylmercapto-3-methylphenyl) thionophosphate,
γ-hexachlorocyclohexane and
(cyclohex-1-ene-1,2-dicarboximidomethyl) 2,2-dimethyl-3-(2-
methylpropenyl)-cyclopropanecarboxylate.

20 The emulsifier mixtures present in the microemulsions
according to the invention consist of either at least one alkyl-
aryl polyglycol ether of the formula (I) and at least one alkyl-
arylsulphonic acid salt of the formula (II), or at least one
alkylaryl polyglycol ether of the formula (III) and at least one
alkylarylsulphonic acid salt of the formula (II).

The alkylaryl polyglycol ethers of the formula (I) are
defined in a general manner by the formula

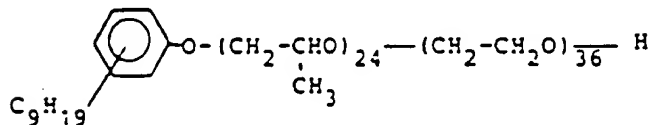
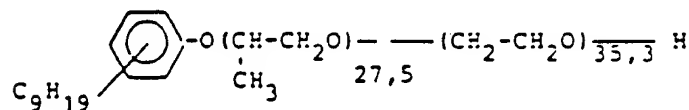
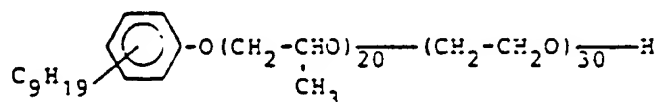
1209361

- 9 -

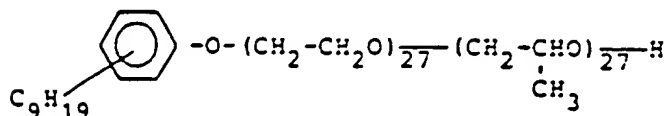
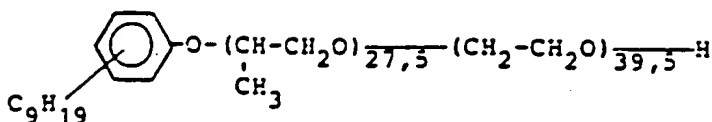
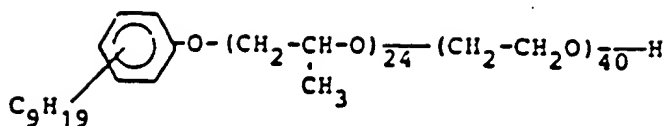
indicated. In this formula, R preferably represents alkyl having 10 to 18 carbon atoms. X and Y each represent a -CH₂-CH₂-O-, -CH₂-CH(CH₃)-O- or -CH(CH₃)-CH₂-O- group, but

X and Y do not simultaneously represent an oxyethylene or oxypropylene unit. The index m preferably represents numbers from 12 to 30 and the index n preferably represents numbers from 12 to 40. The numbers for the indices m and n represent average values.

The emulsifiers of this type which are used in practice are generally mixtures composed of several compounds of the formula (I). In particular, they are mixtures composed of substances of the formula (I), differing in the number of oxyethylene and/or oxypropylene units. Calculation thus also yields fractional numbers as average values for the indices m and n. Substances for which the following average compositions result may be mentioned as examples:

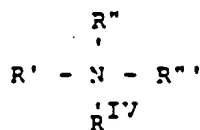


Le A 21 929



The alkylaryl polyglycol ethers of the formula (I)
5 are known.

The alkylarylsulphonic acid salts present in the microemulsions according to the invention are defined in a general manner by the formula (II). In this formula, R^I preferably represents straight-chain or branched
10 alkyl having 9 to 30 carbon atoms. Me[⊕] preferably represents a sodium cation, one equivalent of a calcium cation or a cation of the formula



wherein

15 R^I, R^{II}, R^{III} and R^{IV} independently of one another preferably represent hydrogen, alkyl having 1 or 2 carbon atoms or hydroxyalkyl having 1 to 2 carbon atoms.

The following may be mentioned as individual
20 examples of alkylarylsulphonic acid salts of the formula (II):

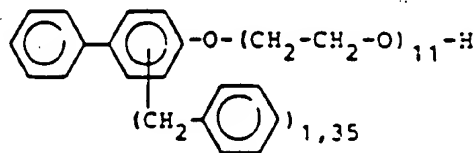
Le A 21 929

sodium 4-(n-nonyl)-phenylsulphonate,
 calcium 4-(n-dodecyl)-phenylsulphonate,
 sodium 4-(tetrapropylene)-phenylsulphonate,
 calcium 4-(n-nonyl)-phenylsulphonate,
 5 ammonium 4-(i-dodecyl)-phenylsulphonate and
 (2-hydroxyethyl)-ammonium 4-(n-dodecyl)-phenylsulphonate.

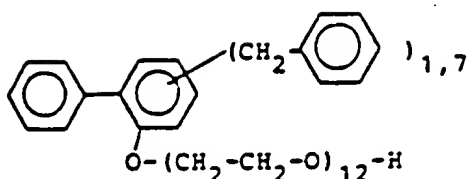
The alkylarylsulphonic acid salts of the formula
 (II) are known. They are generally employed in the form
 of 50-75% strength solutions in organic solvents, for
 10 example n-butanol, i-butanol or benzyl alcohol, but can,
 in principle, also be used without a solvent.

The alkylaryl polyglycol ethers of the formula
 (III) are defined in a general manner by the formula indi-
 cated. In this formula, the index p preferably represents
 15 numbers from 8 to 18, and the index q preferably repre-
 sents numbers from 1 to 2. The numbers for the indices p
 and q represent average values.

The emulsifiers of this type which are used in
 practice are generally mixtures composed of several com-
 20 pounds of the formula (III). In particular they are mix-
 tures composed of substances of the formula (III), differ-
 ing in the number of oxyethylene units and/or in the
 degree of substitution on the phenyl radical. Calculation
 can thus also yield fractional numbers as average values
 25 for the indices p and q. Substances for which the follow-
 ing average compositions result may be mentioned as
 examples:



and



The alkylaryl polyglycol ethers of the formula (III) are also known.

Any customary organic solvents of low miscibility with water are suitable as the organic solvents which can, if appropriate, be present in the microemulsions according to the invention. Solvents which may be mentioned preferentially are aromatic hydrocarbons, such as xylene, toluene and dimethylnaphthalene, and also chlorinated aromatic hydrocarbons, such as chlorobenzenes, and also aliphatic hydrocarbons, such as ligroin and petroleum ether, additionally halogenated aliphatic hydrocarbons, such as methylene chloride and chloroform, additionally cycloaliphatic hydrocarbons, such as cyclohexane, and also alcohols and ketones, such as n-butanol, n-hexanol, isohexanol, n-octanol, cyclohexanol, benzyl alcohol, di-n-butyl ketone and isophorone, and also ethers and esters, such as glycol monomethyl ether and glycol monomethyl ether-acetate, and, furthermore, also triethyl phosphate.

Any customary solubilisers are suitable as the solubilisers which can be present in the microemulsions according to the invention. Solubilisers which can be used preferentially are alkylphenols or cresols which have been subjected to a condensation reaction with, per mol, 1 to 8 mols of ethylene oxide. p-Cresol which has been subjected to a condensation reaction with, per mol, 1 to 8 mols of ethylene oxide should be mentioned specially in this connection.

Suitable additives which can, if appropriate, be present in the microemulsions according to the invention are preservatives, dyestuffs, cold stabilisers and

synergists.

2-Hydroxybiphenyl and sorbic acid may be mentioned as examples of preservatives. Azo dyestuffs and phthalocyanine dyestuffs may be mentioned as examples of dyestuffs. Urea, sugars and salts, such as ammonium sulphate and sodium oleate, may be mentioned as examples of cold stabilisers. 3,4-Methylenedioxy-6-propylbenzyl-n-butyl-diethylene glycol ether (piperonyl butoxide) may be mentioned as an example of a synergist.

10 The percentage proportions of the components present in the microemulsions according to the invention can be varied within specific ranges. In general, the proportion of active compound or active compounds is between 0.1 and 80% by weight, preferably between 5 and 80% by weight. The proportion of emulsifier mixture is, in
15 general, 1 to 20% by weight, preferably 3 to 16% by weight, and the ratio of the emulsifiers to one another can also be varied within a specific range. In general, there is ~~0.2 to 1.2, preferably 0.4 to 1, part of emulsifier of the~~
20 formula (II) to 1 part of emulsifier of the formula (I). Furthermore, there is, in general, 0.1 to 1.2 parts, preferably 0.2 to 1.0 part, of emulsifier of the formula (II) to 1 part of emulsifier of the formula (III).

Organic solvents of low miscibility with water
25 and/or solubilisers can be present in proportions of 1 to 30% by weight, preferably 5 to 20% by weight. Additives can be present in proportions of 0.05 to 15% by weight, preferably 0.1 to 10% by weight. The percentage proportion of water in the microemulsions according to the
30 invention is in each case the difference between 100% by weight and the total of the percentage proportions of the other components.

The ratio of active compound(s), on the one hand, optionally mixed with organic solvents and/or solubilisers,
35 to the emulsifier mixture on the other hand can be varied within a specific range in the microemulsions according to
Le A 21 929

the invention. In general, there are 1 to 15 parts by weight, preferably 2 to 10 parts by weight, of active compound(s), if appropriate mixed with organic solvents and/or solubilisers, to 1 part of emulsifier mixture.

5 In preparing the microemulsions according to the invention it can be preferable to use all the components which have already been mentioned preferentially in connection with the description of the microemulsions according to the invention.

10 If an active compound which is in the liquid state at temperatures up to 40°C is used in the process according to the invention, it is generally unnecessary to add an organic solvent and/or a solubiliser of low miscibility with water.

15 If, on the other hand, an active compound which is in the solid state at temperatures up to 40°C is used in the process according to the invention, it is necessary to dissolve the active compound concerned in an organic solvent of low miscibility with water and/or a solubiliser
20 before emulsification. The quantity of organic solvent and/or solubiliser in this case is such that it is exactly sufficient to dissolve the solid substance.

The reaction temperatures in the process according to the invention can be varied within a fairly wide range.
25 In general, the process is carried out at temperatures between 10°C and 80°C, preferably between 20°C and 60°C.

The method generally followed in carrying out the process according to the invention is first to prepare a homogeneous solution consisting of one or more active compounds, an emulsifier mixture, if appropriate an organic
30 solvent of low miscibility with water and/or a solubiliser and, if appropriate, additives, and then to add this mixture, while stirring, to water, if appropriate containing additives. In doing so, the quantities of the components
35 are selected in such a way that the components in the resulting microemulsion are present in the concentration
Le A 21 929

desired in the particular case. The sequence in which the components of the organic phase are combined can be varied. The addition of the organic phase to the aqueous phase is advantageously effected slowly, while stirring uniformly with customary stirring equipment. In the course of this, a finely disperse, transparent microemulsion which can no longer be distinguished optically from a solution, is formed.

The microemulsions according to the invention can be applied either in the form in which they have been prepared or after prior dilution. The quantity applied depends on the concentration of the active compounds in the microemulsion and on the particular indication.

The use of the microemulsions according to the invention is effected by the customary methods, that is to say, for example, by spraying, sprinkling or pouring.

The preparation of the microemulsions according to the invention can be seen from the following examples.

Preparation Examples

20 Example 1

- 8 g of an emulsifier mixture consisting of
6 parts by weight of a nonylphenol polyglycol ether which has an average of 27 oxyethylene and 27 oxypropylene units per molecule,

25 and

- 4 parts by weight of calcium 4-(n-dodecyl)-phenylsulphonate (dissolved in n-butanol),

is added, at temperatures between 20°C and 40°C and while stirring, to 70 g of the insecticidal active compound 30 0,0-dimethyl 0-(4-methylmercapto-3-methylphenyl) thionophosphate. The homogeneous solution thus formed is poured, in the course of 2 minutes and while stirring vigorously, into 22 g of deionised water. When the addition is complete, stirring is continued for a further 5 minutes. A 35 transparent microemulsion is formed, which exhibits no physical or chemical changes even after storage at elevated

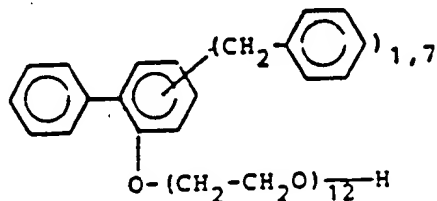
1209361

- 16 -

temperature for several weeks.

Example 2

Example 2
14 g of an emulsifier mixture consisting of
- 10 parts by weight of an alkylaryl polyglycol
ether, the average composition of which can be
5 seen from the following formula



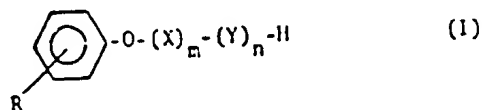
and

and
- 4 parts by weight of calcium 4-(n-dodecyl)-
phenylsulphonate (dissolved in n-butanol),
10 are added, at temperatures between 20 and 40°C and while
stirring, to 50 g of O,O-dimethyl O-(4-methylmercapto-3-
methylphenyl) thionophosphate. The homogeneous solution
thus formed is added, in the course of 2 minutes and while
15 stirring vigorously, to 36 g of deionised water. When the
addition is complete, stirring is continued for a further
5 minutes. A transparent microemulsion is formed, which
exhibits no physical or chemical changes even after
storage at elevated temperature for several weeks.

1209361

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An aqueous microemulsion comprising:
 - A. 0.1 to 80% by weight of at least one agrochemically active compound of low solubility in water and/or one active compound for combating pests in the household and hygiene sectors, and
 - B. 1 to 20% by weight of a mixture of emulsifiers selected from
 - a) a mixture of at least one alkylaryl polyglycol ether of the formula



in which

R represents alkyl having 8 to 20 carbon atoms,

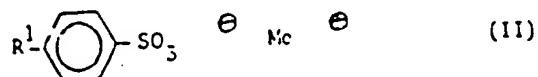
X and Y each represent a $-\text{CH}_2-\text{CH}_2-\text{O}-$,

$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{O}$ or $-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{O}-$ group, but X and Y do not

simultaneously represent an oxyethylene or oxypropylene unit,

m represents numbers from 10 to 45 and

n represents numbers from 10 to 45, with at least one alkylarylsulphonic acid salt of the formula



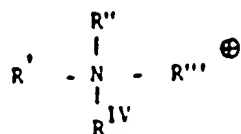
in which

R^1 represents alkyl having 8 to 35 carbon atoms and

Me^+ represents an alkali metal cation, an

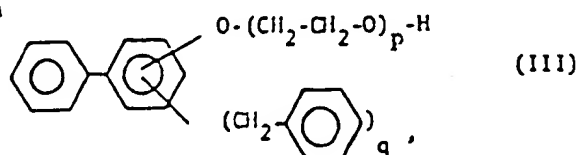
1208361

equivalent of an alkaline earth metal cation
or a cation of the formula



wherein

R', R'', R''' and R^{IV} independently of one another
represent hydrogen, alkyl having 1 to 4 carbon atoms
or hydroxyalkyl having 1 to 4 carbon atoms, or
b) a mixture of at least one alkylaryl polyglycol ether of
the formula



in which

p represents numbers from 5 to 20 and
q represents numbers from 1 to 3, with at least one
alkylarylsulphonic acid salt of formula (II) defined above,
the sum of the recited components and the water being in
each case 100% by weight.

1209361

2. An aqueous microemulsion according to Claim 1, wherein the microemulsion contains 1 to 30% by weight of at least one organic solvent of low miscibility with water and/or a solubilizer.
3. An aqueous microemulsion according to Claim 1, wherein the microemulsion contains 0.05 to 15% by weight of an additive.
4. A microemulsion according to Claim 2, wherein said organic solvent is an aromatic hydrocarbon, chlorinated aromatic hydrocarbon, aliphatic hydrocarbon, chlorinated aliphatic hydrocarbon, alcohol, ketone, ether, ester or trialkyl phosphate.
5. A microemulsion according to Claim 4, wherein said organic solvent is selected from the group consisting xylene, toluene, dimethylnaphthalene, ligroin, petroleum ether, methylene chloride, chloroform, cyclohexane, n-butanol, n-hexanol, isohexanol, n-octanol, cyclohexanol, benzyl alcohol, di-n-butyl ketone, isophorone, glycol monomethyl ether, glycol monomethyl ether-acetate and triethyl phosphate.
6. A microemulsion according to Claim 3, containing as an additive, a preservative, dyestuff, cold stabilizer or synergist.
7. A microemulsion according to Claim 1, wherein component A is an agrochemically active compound.
8. A microemulsion according to Claim 7, wherein said agrochemically active compound is an insecticide, acaricide, nematocide, fungicide, herbicide, plant growth regulator or fertilizer.

9. A microemulsion according to Claim 8, wherein said agrochemically active compound is a compound selected from the group consisting of:

O,O-diethyl O-(4-nitrophenyl) thionophosphate,
 O,O-dimethyl O-(4-nitrophenyl) thionophosphate,
 O-(ethyl) O-(4-methylthiophenyl) S-propyl dithiophosphate,
 (O,O-diethylthionophosphoryl)- α -oximinophenylacetonitrile,
 2-isopropoxyphenyl N-methylcarbamate,
 3-methylthio-4-amino-6-tert.-butyl-1,2,4-triazin-5-one,
 3-methylthio-4-isobutylideneamino-6-tert.-butyl-1,2,4-triazin-5-one,
 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine,
 2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate,
 3,5-dimethyl-4-methylthiophenyl N-methylcarbamate,
 O,O-diethyl O-(3-chloro-4-methyl-7-coumarinyl) thiophosphate,
 6,7,8,9,10,10-hexachloro-1,5,5A,6,9,9A-hexahydro-6,9-methane-2,3,4-benzodioxathiepin-3-oxide,
 1,4,5,6,7,8,8-heptachloro-4,7-endomethylene-3A,4,7,7A-tetrahydroindene,
 2-(2-furyl)-benzimidazole,
 5-amino-1-bis-(dimethylamido)-phosphoryl-3-phenyl-1,2,4-triazole,
 4-hydroxy-3-(1,2,3,4-tetrahydro-1-naphthyl)-coumarin,
 S-[1,2-bis-(ethoxycarbonyl)-ethyl] O,O-dimethyl dithiophosphate,
 O,O-dimethyl O-(4-methylmercapto-3-methylphenyl) thionophosphate,
 O-ethyl-O-(2-isopropoxy-carbonylphenyl)-N-isopropylthiono-

LIQUID ACTIVE INGREDIENT CONCENTRATES FOR PREPARATION OF MICROEMULSIONS

The invention concerns new active ingredient formulations as claimed in claims 1-8, and their application for the production of so-called microemulsions, in which the lipid phase is present with a fineness of 10-200 nm.

Many active effective substances, e.g. pharmaceutical active substances or pesticides, are poorly soluble or insoluble in water, making it impossible to produce homogeneous liquid forms of application.

DE-OS No. 30 42 365 describes liquid, single-phase multi-substance systems containing lecithin, which systems contain active ingredients that are poorly soluble or insoluble in amphiphilic phospholipids. The system contains viscosity regulators in the form of glycerine esters of fatty acid and/or acylated and/or methoxylated derivatives of these glycerine esters or polyether glycols. The systems are shiny, oily liquids.

These liquids cannot, however, be diluted with water to form stable, finely divided emulsions—so-called microemulsions; instead the result is separations, precipitations, and non-homogeneous systems.

The objective of the invention is to create homogeneous, liquid, active ingredient formulations with active ingredients that are insoluble or poorly soluble in water, formulations which can be diluted with any quantity of water and thus, as application preparations, form homogeneous, transparent emulsions.

This objective is achieved by the liquid active ingredient formulations described in the patent claims and by their application in the production of microemulsions.

Surprisingly, it was found that homogeneous, liquid, transparent active ingredient concentrates can be produced with active ingredients that are insoluble or poorly soluble in water, concentrates which can be mixed with water in any ratio.

The liquid active ingredient formulation under the invention is a lipophilic liquid containing phospholipids or phospholipid mixtures, a co-emulsifier, a lipophilic carrier liquid, and the active ingredient. Water can be added to this lipophilic active ingredient concentrate in any quantity without its transparency being lost. This creates application formulations which contain the active ingredient(s) in homogeneous form in a lipid phase; the active ingredients are present in this preparation, which is ready for application, in the form of O/W microemulsions, with a particle or micro-droplet size of 10-200 nm. These transparent emulsions, or, as understood in this invention, application preparations, which result from the dilution of the lipophilic concentrates with water, can involve micellar dispersions as well as microemulsions, in which the droplet size in the dispersion phase has a colloidal magnitude (Leon M. Price, Microemulsions, Academic Press, Inc.).

The phospholipids employed in the invention concentrate formulations can be mixtures of phosphatidyl choline, phosphatidyl ethanol amine, N-acylphosphatidyl ethanol amine, phosphatidic acid, or phosphatidyl inositol, particularly phospholipids with a phosphatidyl choline content of 30-95%.

The co-emulsifier can be glycerin in which the 1 or 2 OH groups have been esterized by means of saturated fatty acids with hydrocarbon chains of 8-16, preferably 8-10 C atoms, and the third or remaining OH group of the glycerin body is etherized with polyethylene glycol,

specifically with 6-30, preferably 6-15, ethylene oxide units. The HLB values of these co-emulsifiers (following Griffin) are between 12 and 18, preferably between 15 and 17.

Examples of these co-emulsifiers are a water-soluble partial glyceride mixture of natural, saturated vegetable oil acids of moderate chain length, in the form of a viscous oil, re-esterized polyethoxylized caprylic acid/-capric acid glyceride (PEG-6-caprylic acid/capric acid glyceride, polyoxyethylene-glycerin monolaurate with HLB 15.7, polyoxyethylene-glycerin ricinoleate with HLB 14).

Suitable carrier liquids are glycerides compatible with phospholipids, to which suitable low esters have been added, particularly fatty acid esters, for example, acetic acid ethyl ester, isopropyl myristate or isopropyl palmitate.

To improve compatibility with the phospholipids, organic solvents can be added, which must be miscible with water at any ratio, for example, lower alcohols with C₁₋₄ carbon atoms, dimethyl formamide, dimethyl amine or 2-dimethyl-4-hydroxy methyl-1,3 dioxalane.

The usual auxiliary agents, such as antioxidants, complex formers, or preservatives, can also be added.

Essential for the formation of microemulsions from the concentrates is the molar ratio of the phospholipid to the co-emulsifier. This ratio can be from 1:1 to 1:4, preferably 1:1 to 1:2. A ratio of 1:2 is particularly recommended. The quantity of carrier liquid also influences the formation of the microemulsion.

The invention active ingredient concentrates from which the application preparations are produced through the addition of certain quantities of water have the following compositions:

5-50 wgt.-% phospholipids
5-80 wgt.-% co-emulsifier
10-60 wgt.-% carrier liquid
0.1-50 wgt.-% active ingredient
0.1-10 wgt.-% other additives and auxiliary agents

To produce the new active ingredient concentrates the phospholipid is dissolved under slight heat in the solvent or solvent mixture while being stirred. The co-emulsifier and other auxiliary agents are stirred into the homogeneous liquid. The active ingredient is then added and stirred under low heat up to a maximum of 60° C. and is stirred until the homogeneous phase is reached. A microemulsion forms from this homogeneous, predominantly lipophilic phase when the liquid is diluted with water, and represents the preparation ready for use.

The active ingredients can be pharmaceutical active substances insoluble in water or plant protectants with a herbicidal, fungicidal, insecticidal, acaricidal, nematocidal effect or with an effect regulating plant growth.

From the group of herbicides, e.g.:

N-phosphone methyl glycin (glyphosat),
3-(2-chloro-4-methyl-phenyl)-1,1-dimethyl urea (chlortoluron),
N-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-aminocarbonyl-2-chlorophenyl sulfonamide,
3-(4-isopropyl-phenyl)-1,1-dimethyl urea (isoproturon),
3-methyl-4-amino-6-phenyl-1,2,4-triazine-5(4H)-on (metamitron),
1,3-dimethyl-3-(2-benzthiazolyl)-urea (methabenzthiazuron),
2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine)
3-(3,4-dichlorophenyl)-1-methoxy-1-urea (linuron),